09/937464
Attorney Docket No. 24448-0030
Express Mail No. 912435168US
JC03 Rec'd PCT/PTO 24 SEP 2001

SILANE-BASED COATING MASS WITH A CATALYTIC, OXIDATIVE AND DEODORIZING EFFECT

The invention relates to a catalytic composition, to a process for preparing it and to the use of the catalytic composition for the purpose of deodorizing and oxidizing organic components or carbon.

An object of the present invention is to provide catalytic compositions which are capable of reducing or eliminating environmental odour pollution (deodorizing) and which are able to oxidize organic components or carbon.

This objective is surprisingly achieved by means of a catalytic composition which comprises a coating of a coating material on a support and is obtainable by applying the coating material, comprising (1) a polycondensate of

(A) one or more silanes of the general formula (I)

$$R_a\text{-Si-}X_{(4-a)} \qquad (I)$$

in which the radicals R are identical or different and are non-hydrolysable groups, the radicals X are identical or different and are hydrolysable groups or hydroxyl groups and a has the value 0, 1, 2 or 3, with a being greater than 0 for at least 50 mol% of the silanes, or an oligomer derived therefrom,

(B) if desired, one or more compounds of glass-forming elements,

and (2) particles of one or more transition metal oxides, the weight ratio of transition metal oxide particles to polycondensate being from 10:1 to 1:10, to the support and subjecting the applied coating material to thermal treatment.

In the hydrolysable silanes (A), the hydrolysable groups X are, for example, hydrogen or halogen (F, Cl, Br or I), alkoxy (preferably C_{1-6} alkoxy, such as methoxy, ethoxy, n-propoxy, i-propoxy and butoxy), aryloxy (preferably C_{6-10} aryloxy, such as phenoxy), acyloxy (preferably C_{1-6} acyloxy, such as acetoxy or propionyloxy), alkylcarbonyl (preferably C_{2-7} alkylcarbonyl, such as acetyl), amino, monoalkylamino or dialkylamino having preferably from 1 to 12, in particular from 1 to 6, carbon atoms.

The non-hydrolysable radicals R may be non-hydrolysable radicals R^1 or may be radicals R^2 which carry a functional group, R^1 being preferred.

The non-hydrolysable radical R^1 is, for example, alkyl (preferably C_{1-8} alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl and t-butyl, pentyl, hexyl, octyl or cyclohexyl), alkenyl (preferably C_{2-6} alkenyl, such as vinyl, 1-propenyl, 2-propenyl and butenyl), alkynyl (preferably C_{2-6} alkynyl, such as acetylenyl and propargyl) and aryl (preferably C_{6-10} aryl, such as phenyl and naphthyl). The stated radicals R^1 and X may if desired have one or more customary substituents, such as halogen or alkoxy, for example.

Specific examples of the functional groups of the radical R^2 are the epoxy, hydroxyl, ether, amino, monoalkylamino, dialkylamino, amide, carboxyl, vinyl, acryloyloxy, methacryloyloxy, cyano, halogen, aldehyde, alkylcarbonyl, and phosphoric acid group. These functional groups are attached to the silicon atom via alkylene, alkenylene or arylene bridging groups, which may be interrupted by oxygen or -NH- groups. The stated bridging groups are derived, for example, from the abovementioned alkyl, alkenyl or aryl radicals. The radicals R^2 contain preferably from 1 to 18, in particular from 1 to 8, carbon atoms.

In one preferred embodiment, the silanes (A) comprise a mixture of

(A1) at least one hydrolysable silane of the general formula (II)

$$SiX_4 \qquad (II)$$

in which the radicals X are identical or different and are hydrolysable groups or hydroxyl groups, or an oligomer derived therefrom, and

(A2) at least one organosilane of the general formula (III)

$$R^1{}_{a1}R^2{}_{a2}SiX_{(4-a1-a2)} \qquad (III)$$

in which R^1 is identical or different at each occurrence and is a non-hydrolysable group, R^2 is identical or different at each occurrence and is a radical which carries a functional group, X has the above definition and a1 and a2 have the value 0, 1, 2 or 3, the sum (a1+a2) having the value 1, 2 or 3, or an oligomer derived therefrom

in a molar ratio (A1):(A2) of 5-50:50-95.

In the general formula (III), a1 preferably has the value 1 or 2, a2 preferably has the value 0, 1 or 2 and the sum (a1+a2) preferably has the value 1 or 2.

Particularly preferred hydrolysable silanes (A) and (A1) are tetraalkoxysilanes such as tetraethoxysilane (TEOS). Particularly preferred hydrolysable silanes (A) and (A2) are alkyltrialkoxysilanes, preferably containing C_1-C_8 alkyl, especially methyltriethoxysilane, aryltrialkoxysilanes, especially phenyltriethoxysilane, dialkyldialkoxysilanes, preferably containing C_1-C_8 alkyl, especially dimethyldiethoxysilane, and diaryldialkoxysilanes, especially diphenyldiethoxysilane. Silanes containing functional groups (A) and (A2) are, for example, epoxy silanes such as 3-

glycidyloxypropyltrimethoxysilane (GPTS) and amino silanes such as 3-aminopropyltriethoxysilane and 3-(aminoethylamino)propyltriethoxysilane (DIAMO).

In the silane component (A) according to formula (I), a is greater than 0 for at least 50 mol% of the silanes, i.e. at least 50 mol% of the silanes contain at least one non-hydrolysable group R. The silane component (A) preferably comprises from 50 to 95 mol% of silanes having at least one non-hydrolysable group R. With regard to the formulae (II) and (III), the preferred molar ratio of the hydrolysable silane (A1) to the organosilane (A2) in the polycondensate is 5 to 50:50 to 95, preferably from 1:1 to 1:6 and with particular preference from 1:3 to 1:5. A particularly favourable molar ratio is 1:4.

The optional component (B) constitutes glass-forming elements which are preferably dispersible or soluble in the reaction medium. It is possible to use, for example, compounds (halides, alkoxides, carboxylates, chelates, etc.) of lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, boron, aluminium, titanium, zirconium, tin, zinc or vanadium.

To prepare the polycondensate (1), the starting components (A) and, where appropriate, (B) are hydrolysed and condensed. The hydrolysis and condensation are conducted either in the absence of a solvent or, preferably, in an aqueous or aqueous/organic reaction medium, where appropriate in the presence of an acidic or basic condensation catalyst such as HCl, HNO_3 or NH_3. The hydrolysis and condensation preferably take place in the presence of an aqueous acid. The aqueous acids are used preferably in a concentration range of from 0.1 N to 10.0 N. Acids used with preference are hydrochloric, nitric, phosphoric and acetic acid.

Additionally, during the preparation of the polycondensate, the inorganic particles set out below may be added. During the preparation, preferably, nanoscale inorganic particles, especially in the form of a sol, are added. By way of example, silica sols may act as hydrolytically active compounds in the sol. Suitable for this purpose are commercially customary silica sols, such as the Levasils®, silica sols from Bayer AG, for example.

When a liquid reaction medium is used, the starting components are soluble in the reaction medium. Particularly suitable organic solvents are water-miscible solvents, such as monohydric or polyhydric aliphatic alcohols, for example, but also aliphatic or aromatic hydrocarbons, such as those having from 5 to 20 carbon atoms, ethers, esters, ketones, amides and alkylamides.

The hydrolysis and polycondensation preferably take place under the conditions of the sol-gel process, the reaction mixture being used in the viscous sol state to coat the substrate.

Where appropriate, the hydrolysis and polycondensation are carried out in the presence of a complexing agent, examples of such agents being nitrates, β-dicarbonyl compounds (e.g. acetylacetonates or acetoacetates), carboxylic acids (e.g. methacrylic acid) or carboxylates (e.g. acetate, citrate or glycolate), betaines, diols, diamines (e.g. DIAMO) or crown ethers.

The ratio of the hydrolytically active components to the hydrolysable silanes (and, where appropriate, to the glass-forming elements) may be characterized by the value R_{OR}. The R_{OR} value represents the molar ratio of water from the hydrolytically active components (water, aqueous acid, silica sol, etc.) to the abovementioned hydrolysable groups X from the silane components (and,

where appropriate, the corresponding hydrolysable groups of the glass-forming elements). The sol obtained possesses, for example, an R_{OR} value of from 0.1 to 10 and preferably from 0.2 to 2.

The polycondensate obtained is mixed, preferably in the form of a sol, with particles of one or more transition metal oxides, the ratio of transition metal oxide particles to polycondensate being from 10:1 to 1:10, preferably from 10:1 to 1:1 and with particular preference from 10:1 to 2:1. In the case of this ratio, account is taken for the polycondensate, with the exception of any other organic solvent, of the components added for the purpose of preparing the polycondensate (in particular the inorganic particles for preparing the condensate).

The average particle diameter of the transition metal oxides used is situated, for example, in a range from 10 nm to 20 μm. In the case of coated substrates which are to be used for improving odour, it is preferred to use transition metal oxide particles having an average particle diameter of from 1 to 20 μm.

The particles consist substantially, or preferably completely, of transition metal oxide. The transition metal oxide particles may be composed of one transition metal oxide or of transition metal oxide mixtures. In the case of the transition metal oxide mixtures, which are used with preference, it is preferred to combine different transition metal oxide powders with one another so as to give particles comprising different transition metal oxides. It is of course also possible to use particles which contain different transition metal oxides.

In the case of use for oxidation purposes in particular, however, it is possible, besides the particles consisting essentially of transition metal

oxides, to make additional use, in whole or in part, of particles which have the transition metal oxides indicated below at the surface but which otherwise are composed of a different material. In that case the transition metal oxide particles are composed of particles of a material chosen preferably from one of the materials specified below for the inorganic particles, said material being surface-coated with one or more transition metal oxides. Preferably, these particles are coated fully on the surface with the transition metal oxides. For the weight ratio of transition metal oxide particles to polycondensate, these particles are taken into account as a whole as transition metal oxide particles. The particles in question are in particular the particles in the micrometre range, indicated below, which have been provided on the surface, and/or impregnated, with transition metal oxides.

The transition metal oxides in question are, in particular, catalytically active transition metal oxides which have deodorizing and/or oxidizing properties. By transition metals are meant, as is customary, the elements of transition groups I to VIII of the Periodic Table and the lanthanide and actinide elements. With particular preference the transition metal oxide is selected from the oxides of the metals La, Ce, Ti, Zr, V, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Ag and Zn or from mixtures of these metal oxides. Preference is given to using transition metal oxide mixtures, with mixtures of the oxides of Mn and Ce with one or two further transition metals, such as mixtures of the oxides of Mn/Co/Ce, Mn/Cu/Ce, Mn/Ni/Ce, Mn/Fe/Ce or Mn/Co/Ni/Ce, being particularly preferred. A further-preferred transition metal oxide mixture is a mixture of the oxides of Cu/V/La. It is also possible to use mixed oxides of the aforementioned transition metals.

In the transition metal oxide mixtures, the following amounts of the corresponding metal oxides in the metal oxide mixture are preferred: Ce: 1-70% by weight, V: 5-70% by weight, Mn: 20-95% by weight, Fe: 20-95% by weight, Co: 1-50% by weight, Ni: 1-50% by weight, Cu: 1-95% by weight.

Specific examples of transition metal oxides are MnO_2 (pyrolusite), γ-MnO_2, Co_3O_4, Co_2O_3, CoO and CeO_2. It is of course also possible to use any other suitable transition metal oxide.

The BET surface area of the particles used is situated, for example, within a range from 1 to 100 m^2/g.

Besides the transition metal oxide particles, cocatalysts may also be used in the coating material, in amounts for example of from 1 to 5% by weight, based on the transition metal oxide particles. Suitable cocatalysts are, for instance, K, Mg, Ca, Ba and Sr salts and also Al oxide and Sn oxide. Examples of suitable salts are the corresponding halides, hydroxides, nitrates, carbonates, or phosphates. They may be added, for example, by mixing the cocatalyst with the transition metal oxide particles or with the mixtures of the transition metal oxide particles prior to addition to the polycondensate, or by separate addition of the cocatalyst to the coating material. In the former case, it is preferred to use powders, and in the latter case it is preferred to use readily soluble salts of the cocatalyst.

The coating material may also include inorganic particles, which may be added during the preparation of the polycondensate or of the coating material or thereafter. These particles may be nanoscale inorganic particles or particles in the micrometre range. It is also possible to add particles of both orders of magnitude, in which case the particles in the

micrometre range are employed in particular when the catalytic composition is used for oxidizing organic components or carbon.

The inorganic particles may be composed of any desired materials, with oxides being preferred. Preferred oxides are oxides of Si and Al (especially boehmite). The particles may be added, for example, in the form of powders or, especially the nanoscale particles, in the form of sols.

The nanoscale inorganic particles preferably possess an average particle size of up to 300 nm, in particular up to 100 nm and with particular preference up to 50 nm. The particles may be added in colloidal form. In this case they can comprise sols or dispersible powders. Specific examples of nanoscale inorganic particles are SiO_2, Al_2O_3, SnO_2, iron oxides or carbon (carbon black and graphite), especially SiO_2. Very particular preference is given to using silica sols as nanoscale inorganic particles.

Especially if the catalytic compositions are to be used as oxidative compositions, inorganic particles in the micrometre range may also be added to the coating material. They serve to structure the coating and to produce cavities. These particles possess an average particle diameter of, for example, from 1 to 500 μm, preferably from 10 to 300 μm. They are preferably oxide- and/or hydroxyl-containing compounds of the elements from main groups III and IV, such as aluminium oxides or silicon oxides. They may have been activated. Examples that may be mentioned include kieselguhr, alumina 90, silica gel 40 or silica gel 60, produced by the company Merck.

Prior to their use, the abovementioned inorganic particles in the micrometre range may be impregnated with metal salts or mixtures of metal salts, such as

chlorides, phosphates, formates, nitrates or acetates, and then treated at elevated temperatures in order to generate catalytically active metal oxides on the surface. Preference is given to using metal nitrates or metal acetates, since the anions form volatile products when treated within the temperature range used. Metals used are the transition metals specified for the transition metal oxide particles. In this case particles are obtained which are provided on the surface with transition metal oxides, which are used in accordance with the invention as transition metal oxide particles, and which are taken into account as a whole for the weight ratio of transition metal oxide particles to polycondensate.

The coating material may also comprise further additives. It is possible, for example, to use additives suitable for adjusting viscosity and/or, in particular, for generating cavities during the thermal treatment of the coating materials. For this purpose it is possible, for example, to use customary thickeners. Specific examples are cellulose derivatives, such as hydroxypropylcellulose, starch, modified starch, polyvinyl alcohol and glycols, e.g. polyethylene glycol. Preference is given to using cellulose derivatives, especially hydroxypropylcellulose. In addition it is also possible to use the additives customary in catalytic compositions, such as pigments (e.g. black pigments).

The viscosity of the sol mixed with the transition metal oxide particles may also be adjusted, if desired, by removing or adding a solvent, e.g. one of those mentioned above. In this form, the sol is usually also storable for long periods. Where appropriate, it may be activated by adding water or aqueous acid, in which case the coating material is preferably used within one month.

The coating material is applied to the support by customary coating methods. Applicable techniques are, for example, dipping, flow coating, spin coating, spraying or brushing.

Suitable supports are, for example, those of metals such as stainless steel, steel, copper, brass and aluminium; metal oxides, glasses such as float glass, borosilicate glass, lead crystal or silica glass; glass ceramics, and ceramics such as Al_2O_3, ZrO_2, SiO_2 mixed oxides, or else enamel, but also porous supports such as porous ceramics, for example. The shape of the supports is arbitrary. The supports in question may be planar or structured. Particularly suitable supports are those in the form of meshes, honeycombs or nets, such as wire meshes, examples being steel wire meshes, ceramic honeycombs or wire nets.

The supports may be pretreated prior to the application of the coating material. For example, they are subjected to cleaning, using commercially customary alkaline cleaners, for example. It is likewise possible, for example, by heat-treating steel supports and forming chromium oxide whiskers on the surface, to bring about substantially improved adhesion of the coating material to steel supports.

The resulting coating is subjected to initial drying, if desired, and then heat-treated. This can be done at temperatures of from 200°C to 700°C, preferably from 300°C to 400°C. The heat treatment may be carried out in air on in an inert gas such as nitrogen or argon. The heat treatment may also take place if desired by means of IR or laser radiation. The heat treatment may be accompanied, for example, by drying, curing or consolidation or compaction of the coating material.

The coating operation is preferably performed so as to give coat thicknesses of from 0.01 to 500 µm, preferably from 1 to 500 µm. Where the catalytic compositions are used for the purpose of deodorizing, coat thicknesses of from 30 to 100 µm, in particular from 25 to 75 µm, are preferred. Where the catalytic compositions are used as oxidatively active surfaces, coat thicknesses of from 1 to 10 µm are suitable when using transition metal oxides having an average particle size of less than 200 nm. The catalytic compositions which serve as oxidatively active surfaces, and which additionally comprise inorganic particles in the micrometre range, preferably have coat thicknesses of from 100 to 400 µm.

The catalytic compositions of the invention may have a porous or a non-porous coating. Preferably, the catalytic compositions have porous coatings. The pores may comprise microscopically visible cavities on the surface and/or relatively fine micropores. The cavities visible on the surface under the microscope have an approximately globular morphology (hemispheres) and their diameter is from about 1 to 5 µm. Their extent and form in the interior of the coat cannot be determined by microscopy. The determination of the BET surface areas of preferred embodiments indicates that relatively fine micropores are present therein alternatively or additionally.

The catalytic composition of the invention has a deodorizing effect; in other words, odour pollution caused by substances can be reduced or avoided completely. The deodorizing activity is found in particular at temperatures above 150°C, for example at temperatures from 150 to 500°C, preferably from 200 to 350°C. The odour-polluted air is guided past the catalytic composition at elevated temperatures. As it passes, substances present in the air are degraded.

The catalytic composition is also capable of oxidizing organic components or carbon, such as carbon black or graphite, which are present, for example, on the surface of the catalytic composition. The oxidizing activity is found in particular at the temperature ranges indicated above.

On the basis of these properties, the catalytic composition is preferably employed where odour pollution events may occur or where particularly "odour-neutral" air (that is, air with as little of additional substances as possible) is desirable or where the oxidation of organic components or carbon is desired. In general, the catalytic compositions may be used, for example, in livestock farming, food processing, for example in fish processing or in cheese dairies, in fabrication processes, in waste processing, or generally in chemical industry plants, but also in living spaces. Specific examples of fields of use are therefore toilets of all kinds, baths, means of transport, such as cars, combustion units, especially their exhaust gas installations, e.g. the (diesel) exhaust of a car, caravans, tanks, animal stalls, petrol stations, digestion towers of sewage treatment plants, composting units, manure stations, silos, waste air units of all kinds, gas masks, wardrobes, nappies, refuse containers or gas sensors. The catalytic compositions are preferably used in these fields in such a way that they are located directly on any surface of the article in question, in which case this surface acts as the substrate, or they are located in an additional facility, connected where necessary via a connecting line, within or in the vicinity of the article or of the space within which the articles are located.

EXAMPLES

A. Preparation of the silane sols

Silane sol 1: MTKS sol, R_{OR} = 0.4

A mixture of 1069.86 g (6.0 mol) of methyltriethoxysilane and 312.48 g (1.5 mol) of tetraethoxysilane is divided into two portions (portion 1 and portion 2) of equal weight.

To portion 1, 246.84 g of silica sol (Levasil 300/30, aqueous, basic, Bayer AG) are added with thorough stirring. After an emulsion has formed (about 30 s), 5.60 g of 36% strength by weight HCl are added. After brief stirring (30-50 s) the reaction mixture becomes clear with heating. Portion 2 is added quickly and all at once to this reaction mixture. After a short time, the reaction mixture becomes cloudy owing to a colourless precipitate (NaCl). This is followed by stirring with cooling in an ice bath for 15 minutes. The silane hydrolysate is left to stand at room temperature for 12 h and decanted from the sedimented solid, thus giving the ready-to-use MTKS sol.

Silane sol 2: MDKS sol, ROR = 0.2

35.10 g of silica sol (Levasil 300/30, aqueous, basic, Bayer AG) and 1.10 g of 36% strength by weight HCl are added simultaneously to a mixture of 356.62 g (2.0 mol) of methyltriethoxysilane and 74.14 g (0.5 mol) of dimethyldiethoxysilane, with thorough stirring. After brief stirring (30-50 s) the reaction mixture becomes clear with heating. After a short time, the reaction mixture becomes cloudy owing to a colourless precipitate (NaCl). This is followed by stirring with cooling in an ice bath for 15 minutes. The silane hydrolysate is left to stand at room temperature for 12 h and decanted from the sedimented solid, thereby giving the ready-to-use MDKS sol.

Silane sol 3: MPTKS sol, ROR = 0.4

3.29 g of silica sol (Levasil 300/30, aqueous, basic, Bayer AG) and 0.13 g of 36% strength by weight HCl are added simultaneously to a mixture of 11.59 g (0.065 mol) of methyltriethoxysilane, 3.61 g (0.015 mol) of phenyltriethoxysilane and 4.17 g (0.020 mol) of tetraethoxysilane, with thorough stirring. After brief stirring (30-50 s) the reaction mixture becomes clear with heating. After a short time, the reaction mixture becomes cloudy owing to a colourless precipitate (NaCl). This is followed by stirring with cooling in an ice bath for 15 minutes. The silane hydrolysate is left to stand at room temperature for 12 h and decanted from the sedimented solid, thereby giving the ready-to-use MPTKS sol.

Silane sol 4: MPrTKS sol, ROR = 0.4

7.00 g of silica sol (Levasil 300/30, aqueous, basic, Bayer AG) and 0.23 g of 32% strength by weight HCl are added simultaneously to a mixture of 15.00 g (0.084 mol) of methyltriethoxysilane, 14.95 g (0.091 mol) of n-propyltrimethoxysilane and 8.96 g (0.043 mol) of tetraethoxysilane, with thorough stirring. After brief stirring (30-50 s) the reaction mixture becomes clear with heating. After a short time, the reaction mixture becomes cloudy owing to a colourless precipitate (NaCl). This is followed by stirring with cooling in an ice bath for 15 minutes. The silane hydrolysate is left to stand at room temperature for 12 h and decanted from the sedimented solid, thereby giving the ready-to-use MPrTKS sol.

Silane sol 5: MD sol, ROR = 0.4

5.04 g of 0.1 N HCl are added to a mixture of 35.66 g (0.2 mol) of methyltriethoxysilane and 7.41 g (0.05 mol) of dimethyldiethoxysilane, with thorough stirring. After brief stirring (30-50 s) the reaction mixture becomes clear with heating. The silane

hydrolysate is left to stand at room temperature for 12 h, thereby giving the ready-to-use MD sol.

B. Preparation of the catalyst mixtures

The catalyst mixtures used are mixtures of commercial transition metal oxide powders from Ferro or Aldrich:

MnO_2: Powder from Ferro, predominantly MnO_2 (pyrolusite), with a little γ-MnO_2 and a little MnO_2

Co_yO_x: Powder from Ferro, predominantly Co_3O_4, with a very little CoO

Catalyst mixture 1: Mn/Co/Ce

Catalyst mixture 1 is prepared by intimately mixing 800.00 g of MnO_2, 100.00 g of Co_yO_x and 100.00 g of CeO_2.

Catalyst mixture 2: Mn/Co/Ce

Catalyst mixture 2 is prepared by intimately mixing 800.00 g of MnO_2, 150.00 g of Co_yO_x and 50.00 g of CeO_2.

Catalyst mixture 3: Mn/Cu/Ce

Catalyst mixture 3 is prepared by intimately mixing 650.00 g of MnO_2, 300.00 g of Cu_2O and 50.00 g of CeO_2.

Catalyst mixture 4: Mn/Co/Ni/Ce

Catalyst mixture 4 is prepared by intimately mixing 700.00 g of MnO_2, 100.00 g of Co_yO_x, 150.00 g of NiO and 50.00 g of CeO_2.

C. Preparation of the coating materials

Example 1

1000.00 g of catalyst mixture 1 are stirred at room temperature for 2 h with 300.00 g of silane sol 1 and 233.33 g of ethanol. Then 32.35 g of 10% strength by weight aqueous hydrochloric acid are added for activation (increasing the R_{OR} value from 0.4 to 0.8),

the mixture is stirred at room temperature for at least 2 h, and the ready-to-use coating suspension is obtained.

Example 2

1000.00 g of catalyst mixture 2 are stirred at room temperature for 2 h with 200.00 g of silane sol 1 and 350.00 g of ethanol. Then 23.49 g of 10% strength by weight aqueous hydrochloric acid are added for activation (increasing the R_{OR} value from 0.4 to 0.8), the mixture is stirred at room temperature for at least 2 h, and the ready-to-use coating suspension is obtained.

Example 3

1000.00 g of catalyst mixture 3 are stirred at room temperature for 1 h with 400.00 g of silane sol 2 and 185.00 g of ethanol. Then 47.97 g of 10% strength by weight aqueous hydrochloric acid are added for activation (increasing the R_{OR} value from 0.2 to 0.6), the mixture is stirred at room temperature for at least 4 h, and the ready-to-use coating suspension is obtained.

Example 4

1000.00 g of catalyst mixture 3 are stirred at room temperature for 1 h with 18.00 g of silane sol 3 and 25.00 g of ethanol. Then 1.52 g of 10% strength by weight aqueous hydrochloric acid are added for activation (increasing the R_{OR} value from 0.4 to 0.7), the mixture is stirred at room temperature for at least 2 h, and the ready-to-use coating suspension is obtained.

Example 5

1000.00 g of catalyst mixture 4 are stirred at room temperature for 1 h with 40.00 g of silane sol 5 and 11.00 g of ethanol. Then 4.66 g of 10% strength by weight aqueous hydrochloric acid are added for

activation (increasing the R_{OR} value from 0.4 to 0.8), the mixture is stirred at room temperature for at least 2 h, and the ready-to-use coating suspension is obtained.

D. Coating and heat treatment (especially for deodorizing purposes)

The support material used is steel wire mesh (diameter about 5 cm, height about 1 cm) or ceramic honeycombs. The steel meshes are first of all degreased using a commercial alkaline cleaner and then rinsed thoroughly with deionized water, before being dried at room temperature. The dry steel meshes are subsequently treated at 500°C for 1 h.

Coating takes place by impregnating the steel wire meshes or the ceramic honeycombs in one of the coating materials (coating suspensions) described in section C. The excess coating suspension is removed by blowing with compressed air. After drying at room temperature (2 h), the coating is solidified by heat treatment. For this purpose the coated supports are heated from room temperature to 300-400°C over the course of 1 h, held at 300-400°C for 1 h, and then cooled to room temperature over 6 h.

Alternatively, the heat treatment may also be effected by direct placement of the dried, coated supports into an oven preheated to 300-400°C and rapid cooling of the hot supports to room temperature over a few minutes.

The thicknesses of the thermally solidified coats are typically in the range 25-75 µm. The coat thicknesses may be set, for example, on the one hand by way of the viscosity of the coating suspension (which can be adjusted, for example, by adding an appropriate amount of ethanol), on the other by way of the pressure of the compressed air or the time of action of the compressed air during removal of the excess coating suspension.

E. Catalytic composition 1 (especially for oxidizing)

E.1 Preparation of an Mn/Cu/Ce catalyst on alumina particles

40.47 g (0.141 mol) of $Mn(NO_2)_2 \cdot 6\ H_2O$, 11.63 g (0.050 mol) of $Cu(NO_3)_2 \cdot 3\ H_2O$ and 15.20 g (0.035 mol) of $Ce(NO_3)_3 \cdot 6\ H_2O$ are dissolved in a mixture of 30.00 g of ethanol and 30.00 g of water at 50°C. 100.00 g of alumina 90 (active, acidic (alternatively, neutral or basic can also be used), particle size 63-200 µm, from Merck) are added to this solution and the solvent mixture is evaporated off with stirring at 50-70°C for 3 h. The alumina impregnated with the metal nitrates is subsequently treated at 500°C for 1 h. Analogously, it is also possible to use the corresponding molar amounts of metal acetates or, instead of aluminium 90, the further Merck products silica gel 40, particle size 63-200 µm, silica gel 60, particle size 63-200 µm, or kieselguhr, particles size approximately 100 µm.

E.2 Coating material

150.00 g of the above-described Mn/Cu/Ce catalyst (E.1) on the alumina particles are intimately mixed with 50.00 g of catalyst mixture 1. 100.00 g of a 5% strength by weight solution of hydroxypropylcellulose in ethanol are added with stirring to this mixture. 140.00 g of silane sol 2 are activated (increasing the R_{OR} value from 0.2 to 0.8) by addition of 22.67 g (1.26 mol) of water, with stirring, and the mixture is stirred at room temperature for 30 minutes. The activated MDKS sol is added to the above-described mixture of Mn/Cu/Ce catalyst, catalyst mixture 1 and hydroxypropylcellulose in ethanol, at room temperature with stirring, and the mixture is then stirred at room temperature for 15 minutes to give the ready-to-use coating material.

E.3 Coating and thermal solidification

The support material used is steel substrates (metal panels 10 × 10 cm). The steel substrates are first of

all degreased using a commercial alkaline cleaner, then rinsed thoroughly with deionized water, and subsequently dried at room temperature. The dry steel substrates may then be treated at 500°C for 1 h.

The cleaned, or cleaned and heat-treated, steel substrates are flooded with the coating material. The coated steel substrates are dried at room temperature for 1 h, then heated from room temperature to 500°C over 1 h, held at 500°C for 1 h, and then cooled to room temperature over 6 h.

The thicknesses of the thermally solidified coats are typically in the range 150-400 μm, depending on the support material used and the amount of coating material used.

F. Catalytic composition 2 (particularly for oxidizing)

F.1 Preparation of a mixed oxide catalyst by coprecipitation of Mn/Co/Ce

121.42 g (0.423 mol) of $Mn(NO_3)_2 \cdot 6\ H_2O$, 14.55 g (0.050 mol) of $Co(NO_3)_2 \cdot 6\ H_2O$ and 9.42 g (0.022 mol) of $Ce(NO_3)_3 \cdot 6\ H_2O$ are dissolved in 350.00 g of water at 80-90°C. The precipitating reagent used is a solution of 66.77 g (1.19 mol) of KOH in 300.00 g of water to which 1.60 g of Tween 80 (polyoxyethylene(20)sorbitan monooleate from Aldrich) and 1.60 g (0.012 mol) of 1-octanol are added with stirring. The above-described solution of the metal nitrates is admixed with the above-described precipitating reagent over 5 minutes at 80-90°C with stirring. The homogeneous, loam-coloured suspension thus obtained is stirred at 90°C for 2 h more and then filtered to remove the precipitate, which is washed twice with 150 g of water each time and once with 50 ml of ethanol. The precipitate is initially dried at 70°C for 1 h and then heated from room temperature to 600°C

over 1 h, held at 600°C for 2 h, and then cooled to room temperature over 2 h.

The greenish powder obtained in this way is suspended in 250.00 g of water at 90°C and then, following the addition of 1.60 g of Tween 80 and 1.60 g (0.012 mol) of 1-octanol, it is redispersed over the course of 30 minutes using an ultrasonic disintegrater. It is then filtered to remove the precipitate, which is washed twice with 50 g of water each time and once with 100 g of ethanol. The precipitate is initially dried at 70°C for 1 h and then heated from room temperature to 250°C over 1 h, held at 250°C for 1 h, and then cooled to room temperature over 2 h. This gives a fine, greenish catalyst powder.

F.2 Coating material

3.00 g of silane sol 2 are activated (increasing the R_{OR} value from 0.2 to 0.8) by addition of 0.48 g (0.027 mol) of water with stirring, and the mixture is stirred at room temperature for 30 minutes. 10.00 g of the catalyst powder described in section F.1 and 8.00 g of ethanol are added to the activated MDKS sol with stirring, and the mixture is stirred at room temperature for 30 minutes to give the ready-to-use coating material.

F.3 Coating and thermal solidification

The support material used is steel substrates (metal panels 10 × 10 cm). The steel substrates are first of all degreased using a commercial alkaline cleaner, then rinsed thoroughly with deionized water, and subsequently dried at room temperature. The dry steel meshes may then be treated at 500°C for 1 h. The cleaned, or cleaned and heat-treated, steel substrates are flooded with the coating material. The coated steel substrates are dried at room temperature for 1 h, then heated from room temperature to 300-600°C over 1 h,

held at 300-600°C for 1 h, and then cooled to room temperature over 6 h.

The thicknesses of the thermally solidified coats are typically in the range 1-10 µm, depending on the amount of coating material used.

G. Evaluation

Method of determining the deodorizing activity

About 100 mg of the following test substances are introduced into a circulating-air oven preheated to 300°C (catalyst temperature about 300°C, support: steel wire mesh):
pyrazine, thiazole, maltol, vanillin and 2,4-decadienal.

The test substances evaporate in the hot oven, with the vapours being passed as off-gases (off-gas flow: 0.5-1.2 l/s) by the stream of circulating air through an outlet port without a catalyst and an outlet port with catalyst to a downstream sample collector. The collected samples are analysed by means of GC-MS spectroscopy. The spectra are used to determine breakdown rates for the test substances in the off-gas stream that passes over the catalyst in comparison to the off-gas stream which does not pass over a catalyst (principle: relative measurement on an experimental system). The breakdown rates are indicated below in %.

Catalyst	Pyrazine	Thiazole	Maltol	Vanillin	Decadienal
Pd/Pt cat(*1)	0	0	90	90	-
(*2)	83	88	73	78	65
(*3)	69	56	74	70	-

(*1): Palladium, metallic, on steel wire nets, commercial catalyst

(*2): Inventive Mn/Co/Ce-MTKS sol cat., coating material of Example 1

(*3): Inventive Mn/Cu/Ce-MDKS sol cat., coating material of Example 3.

It is found that the catalytic compositions of the invention are capable of breaking down not only the other test substances but also heterocycles such as pyrazine and thiazole. This is not possible with commercially customary palladium catalysts. Also, with the catalytic compositions of the invention, there is no loss of catalytic activity after ten test cycles. In contrast, the commercially customary palladium catalyst is poisoned by heterocycles such as thiazole, losing catalytic activity with time.

Evaluation of the oxidizing capacity

[Test method according to DIN 51 171, "Testing of the self-cleaning capacity of continuously self-cleaning enamel coatings"]

Defined amounts (in each case 20-25 mg) of soya oil or engine oil are applied dropwise to the samples under investigation, at five points located on a circle, and after each dropwise addition are burnt by a one-hour heat treatment at 250°C, until a visible lustre appears as a result of the accumulation of unburned residues. The number of cycles until lustre occurs is used for the assessment.

Coating	Oil	Number of cycles to lustre
(*1)	Soya	4-5
(*2)	Soya	15-17
(*3)	Soya	13-15
(*4)	Engine	10-12

(*1): Commercially customary, oxidative enamel, containing Fe/Mn oxides

(*2): Catalytic composition 1

(*3): Catalytic composition 1, but using silica gel 40 as support material instead of alumina 90

(*4): Catalytic composition 2, e.g. for the firing land (between piston ring top and piston top) of engine pistons.

The catalytic compositions of the invention (coat thicknesses between 150-400 micrometres) possess high absorbency, owing to the cavities which exist in the coating, and hence have a good spreading capacity for oils. In contrast, the glass-like enamels have a low absorbency and spreading capacity.